

The Soil and Groundwater Remediation with Zero-Valent Iron Nanoparticles



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1 Introduction

The present study was organized and planned in order to understand the behavior of the nanoparticles of zero-valent iron (nZVI) when applied in the natural environment where the soil was contaminated by heavy metals. The main knowledge about the nZVI behavior is mostly dedicated to the organic solvents; however, the intention of this project was to test the effective reaction of the nanoparticles in contaminated environments, taking into account the geological context and the target contaminating elements, but also all the logistical and technical aspects that a decontamination intervention of this type involves.

It was not intended, with this project, to study in detail all the chemical processes associated with the chemical reactions that may be involved. The main objective was focused on the effectiveness of the applied methodology, and the possible replication in other geological and chemical contexts.

The possibility of mobilizing less logistical means, no soil mobilization needed due to its in situ treatment and the option of changing its future use in a different industrial context, were the objectives of this project. The simplification of the processes and environmental protection by the minimization of side effects were also considered.

The Barreiro Industrial area, currently managed by the Baia do Tejo Society, is of vital importance in the context of maritime and river transport and consequently on the financial aspects that an infrastructure of this nature brings to the region. Despite the successive improvements that this old industrial area has been suffering,

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there are deep scars in terms of environmental liabilities and any intervention to make this industrial space will involve, not only improving the access conditions and port infrastructure, but also the need of a careful soils management.

Despite the superficial removal of old deposits of ash and pyrite slag that occurred between the years 2008 and 2010, contaminated subsurface soils, with laboring residues, remained on this extensive industrial area.

The groundwater level reveals the presence of several of those contaminants, resulting from the continuous leaching that these contaminants have been suffering over the years. The groundwater level varies between 4.5 and 5.0 m below the ground surface, due to the proximity of the Tagus River.

The migration of the contaminants dissolved in the groundwater creates a significant environmental problem in this old industrial site, moving continuously to the Tagus river, affecting also the surrounding aquifer areas. The absence of effective decontamination measures allowed the maturation phenomenon of those contaminants in the environment, delaying the soil's treatment and consequently of their existing aquifers. The environmental impact, whether by these soils removal for hazardous or non-waste landfill, or treatment centers, or by the incapability, without prior treatment, to reuse these soils in construction processes, has led to this concern being addressed in a different way, using alternative methodologies for the remediation of those contaminated soils. The use of specific nZVI technology, which promotes the soil and groundwater decontamination, avoiding the soils removal, enhancing a minimum environmental impact with a maximization of the remediation process, is thus a clear advantage.

The creation/installation of reactive barriers that would limit the pollutants mobilization and could keep low their respective concentrations in case of continuous mobilization, were also the objectives of this project.

Several countries in Europe, but not limited to, have a positive track record, where several patents have been implemented (e.g., Nanoiron[®]), and where the soils remediation using nZVI is an emerging technology.^{1,2}

In Portugal this new green technology made the first steps, under an investigation and experimental process performed in Barreiro's industrial area. In the present report, the methodology, the obtained data, and further conclusions are presented.

2 The Zero-Valent Iron Nanoparticles

The soil's remediation with the nanoparticles is based on the application of an aqueous suspensions to change the structure and/or degrade contaminants in soil and/or groundwater. Several definitions for the term "nanoparticle" can be found as a

¹ <https://nanoiron.cz/en/application>.

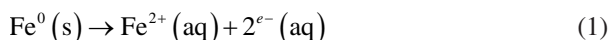
² <https://nanoiron.cz/en/news>.

particle having one or more dimensions of 100 nm or less, which can be written as 10^{-9} m [1].

Nanoparticles of $\text{Fe}^{(0)}$ have recently become a strategic material with great application potential in the broad range of modern nanotechnologies. Due to their extraordinary reduction capabilities (Fig. 1), small size in the range of several tens of nanometers, and high reactivity with a broad spectrum of toxic substances, these ultrafine particles are highly applicable in the reduction technologies of groundwater remediation and wastewater treatment.

In comparison with other frequently used procedures for water treatment, the treatment exploiting of $\text{Fe}^{(0)}$ nanoparticles represents environmentally friendly technology since non-toxic and nature-abundant iron oxides (mainly magnetite— Fe_3O_4) are the products of transformation of $\text{Fe}^{(0)}$.

This Fig. 1 also shows the porosity of the nanoparticle, which is also an important factor in physicochemical reactivity. Zero-valent nano-iron can also be coupled with trace metals (e.g., Pt, Pd, Ag), showing significantly enhanced reaction. Nano-iron is potentially benign to the environment and, ultimately, is mainly transformed into Fe_3O_4 and Fe_2O_3 , which are abundant on earth (Copyright © 2007 GeoNano Environ. Tech., Inc., in [1]). Elemental iron slowly oxidizes to ferrous iron and releases two electrons. These electrons begin to function in a variety of reactions that lead to the transformation of target contaminants. In the environment and in accordance with the half reaction (Eq. 1), elemental iron is oxidized by several substances under the following oxidations half reaction.



NANOFER 25S[®] was applied for the Barreiro project. An inorganic and a biodegradable organic modifier were added as stabilizers for the dispersion of the $\text{Fe}^{(0)}$ in an aqueous form. The zero-valent iron nanoparticles have, in average, a size of

Fig. 1 Schematic three-dimensional presentation of the nZVI regarding the double effect of reduction process and adsorption of the heavy metal on its surface. (Copyright © 2007 GeoNano Environ. Tech., Inc., in [1])

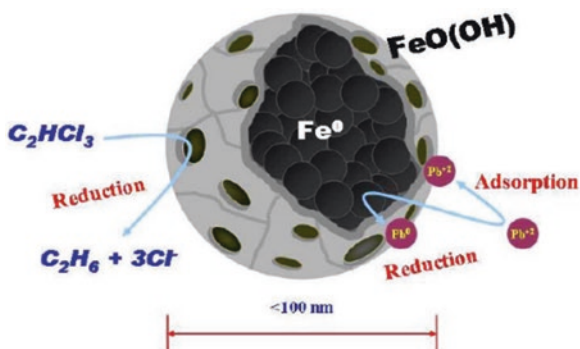


Table 1 Nano zero-valent iron specifications

NANOFER25S [®] chemical composition	Core (Fe)/Capsule (FeO)
Shape of the particle	Spherical
Solid fraction (FeO mass)	80%
Solution density	1210 kg/m ³
Solution (%/mass)	20%
Substances (liquid fraction)	Organic stabilizer
Substances (solid fraction)	FeO, Fe ₃ O ₄ , C
Particle size (FeO)	d50 nm < 50
Color	Black
Density (FeO)	7870 kg/m ³
Density (Fe ₃ O ₄)	5700 kg/m ³
Specific surface	>25 m ² /g

50 nm, the surface area varies between 20 and 25 m²/g, a high content of iron between 80 and 90 wt%,³ and a particle size distribution of 20–100 nm.

The NANOFER25S[®], giving the producer⁴ data, has the following composition summarized in Table 1.

2.1 The Environmental Impact of the Use of Nanoparticles

The European NanoRem project⁵ addressed this issue and as part of the project, increasing knowledge, confidence and providing regulators and other stakeholders evidences whether the technology is environmentally harmful to the natural ecosystem functions of soil and groundwater. Uncertainties about the environmental impact of reactive nanoparticles' use to ecosystems is identified as a key factor to the restricted use of them in soil and groundwater remediation. According to recent NanoRem's investigation group press release, no significant toxicological effects were found on soil or water organisms when ecotoxicological tests were undertaken for a range of nanoparticles that could be used for remediation projects, namely *NanoFer 25S*, made from nanoscale zero-valent iron; *Carbo-Iron*, a composite made from activated carbon and zero-valent iron; *Fe-Oxide*, nanoscale goethite and *Fe-Zeolites*, aluminosilicate containing an iron catalyst.⁶ Nanoparticles were tested for their effects on a range of organisms, mostly using standard methods published, e.g., by the Organization for Economic Co-operation and Development (OECD).⁷

³ <http://www.nanoiron.cz/en/characteristics-of-iron-nanoparticles>.

⁴ www.nanoiron.cz.

⁵ <http://www.nanorem.eu/Displaynews.aspx?ID=824>.

⁶ <http://www.nanorem.eu/displayworkpackage.aspx?id=3>.

⁷ <http://www.nanorem.eu/displayworkpackage.aspx?id=5>.

Ecotoxicity testing will continue for any new nanoparticles or formulations developed as the NanoRem project progresses. The project has also been looking at how nanoparticles reactivity and toxicity change with time. It is believed that as nanoparticles interact within the soil matrices they become less reactive, and therefore less toxic with time. NanoRem's findings confirm this anticipated trend which is similar to how chemicals react in soil. As chemical contaminants age in the soil, their reactivity is reduced along with their bioavailability and toxicity.

3 The Tested Area Framework

The investigation program was conducted inside a brownfield site, located in southern Lisbon, in the left bank of the Tagus River (Fig. 2), in the town of Barreiro, between December 2010 and November 2011. Given the estuarine conditions, the tidal effect influences the water table intersected in the test area, which is positioned approximately 4.5–5.0 m deep, from the ground surface.

3.1 *Geologic and Hydrogeological Local Context*

The ground of the testing area belongs to the Pliocene detrital formations (PSM-Formação de Santa Marta; [2]) (Fig. 2).

From the base to the top occurs a discontinuous conglomerate layer, followed by fine to coarse arkosic sand of fluvial genesis. The colors range from white to red or yellow. Blocks of Cretaceous sandstones and chert nodules occur within the sands. Kaolinite and illite predominate in the clay fraction.

Boreholes performed in this area intersected coarse to fine yellow to orange sand, with a silty-clay matrix, and some interbedded centimetric clay levels with reddish color [3].

In terms of effective porosity, sustained in the fact that the local soils are mainly coarse and medium sands with silt and clays, a value of 15% [4] was considered.

This area is part of the left margin aquifer system of the Tagus-Sado Basin, a multi aquifer, free, confined or semi-confined, where the lateral and vertical facies variations are responsible for significant changes in hydrogeological conditions.

Given the proximity of the mouth of the Tagus River, occurs in the testing area the influence of tidal effect on the groundwater level, which is positioned between 4.0 and 5.0 m deep. The observations of the tidal effect on the piezometric levels in the tested area allowed estimating the hydraulic diffusivity of the aquifer.

The determination of the hydraulic diffusivity in confined aquifers is possible thanks to the work of Jacob [5], Ferris [6], van der Kamp [7], and de Cazenove [8]. The latter also presents solutions for semi-confined aquifers. Regarding the free aquifers, the development of appropriate solutions to describe the tides propagation phenomenon has been the subject of recent work: Ataie-Ashtiani et al. [9, 10], Chen



Fig. 2 Location of the Barreiro site area in the geological map. (Extract from the Portuguese Geological Map – Part 34-D from Lisbon, scale 1:50,000)

et al. [11], Li and Jeng [12], Li and Jiao [13], Pandit et al. [14], Smith and Hick [15], and Wang and Tsay [16]. A summary of different studies and methods that analyze this phenomenon can be found in Li and Jiao [17].

Almeida and Silva [18] applied the equations previously developed in Algarve aquifers. The diffusivity can be obtained from the aquifer oscillations amplitude or from the discrepancy between the maximum (or minimum) of the tide and the maximum (or minimum) of the aquifer oscillation.

From the ratio between amplitudes, the diffusivity can be obtained by the expression:

$$D = \frac{x^2 \pi}{t_0 \cdot \ln^2 (\Delta h_0 / \Delta H_0)} \tag{2}$$

From the discrepancy, the following expression can be used:

$$D = \frac{x^2 t_0}{4\pi t_L^2} \tag{3}$$

where D is the diffusivity (m^2/h), x the distance between the piezometer and the coast, t_0 the tide period, t_L the discrepancy (h), Δh_0 and ΔH_0 , the oscillation semi-amplitudes in the piezometer and tide, respectively.

Although the tide results from the combination of several harmonics, short period of observation is sufficient to consider the most important one, with a period of 745'.

The expression given by de Cazenove [8]:

$$D = \frac{x^2}{2t_L \cdot |\ln(\Delta h_0 / \Delta H_0)|} \tag{4}$$

allows to obtain the diffusivity by simultaneously using the amplitude and discrepancies.

In this case it is possible to obtain an additional parameter, ρ , related with the drenancy factor, $\lambda = \sqrt{KBB' / K'}$, where K is the aquifer hydraulic conductivity, K' is the aquitard hydraulic conductivity, B is the thickness of the aquifer, and B' is the thickness of the aquitard $x_0 = \sqrt{Tt_0 / \pi S}$,

$$\rho^2 - 1 / \rho^2 = x_0^2 / \lambda^2 \tag{5}$$

In order to obtain a better accuracy in the determination of the oscillation amplitude in the river and piezometer, and the discrepancies between the maximum (or minimum) in both locations, equivalent sinusoids were adjusted.

From the ratio between amplitudes and the discrepancies value, diffusivity calculations were performed assuming a 580 m distance between the testing area and the river. This distance is only an approximation given the irregular contour of the river front in the nearest area of the site test.

The equivalent sinusoids were obtained by a nonlinear optimization method, minimizing the squares of the differences between the observed values and the corresponding values of the equivalent sinusoid (MARSINUS program, Almeida and Silva [18]).

According to Caldeira et al. [3], the diffusivity of this aquifer system, considering the drenancy, is 18.344 m^2/h , the drenancy factor is 432 m^2 , and ρ is 2.1416. The obtained result is compatible with a hydraulic conductivity of 5×10^{-5} m/s (equivalent to 0.18 m/h), a 10 m thickness, and a storage coefficient of 10^{-4} .

The obtained diffusivity value is clearly compatible with a semi-confined aquifer system.

Groundwater studies defined the local hydrological system as an aggressive environment due to its low pH varying between 2.9 and 4.1, which is mainly related with the ground and groundwater high concentration of sulfates.

4 The Site Investigation

In the area where the tests took place, an industrial complex worked for more than a half-century, having as its core business the manufacture of fertilizers and sulfuric acid (from massive polymetallic sulfides). The in situ methodology of soil and groundwater remediation used zero-valent iron nanoparticles (nZVI) NANOFER25S [3] (Fig. 3).

According to the available data, the area where the pilot tests were conducted has an industrial background with a strong presence of heavy metals, namely zinc, copper, lead, arsenic, sulfates, and nitrates. The implementation of the in situ testing was preceded by the physical and chemical characterization of soils, groundwater, and lixiviates produced by contaminated soils.

Some of the recorded values significantly exceed the concentrations considered to limit the use of land, requiring that it will be transported to landfill of hazardous waste, dangerous or not depending on the effective concentration of the different compounds.

The soil's contaminants presence investigation, was also performed in water samples taken in the piezometers installed in the various testing areas, working as blank values for further comparison after the application of nZVI.

With the perspective of being able to reduce or minimize the presence of these compounds in that soil matrix, or even to stabilize their chemical behavior in order to reduce the leaching process and the presence in the aqueous phase, it was developed the remediation project with the use of nZVI. The implementation plan and respective control will be described in the following chapters.



Fig. 3 General view of the pilot area, inside de Barreiro Industrial Park

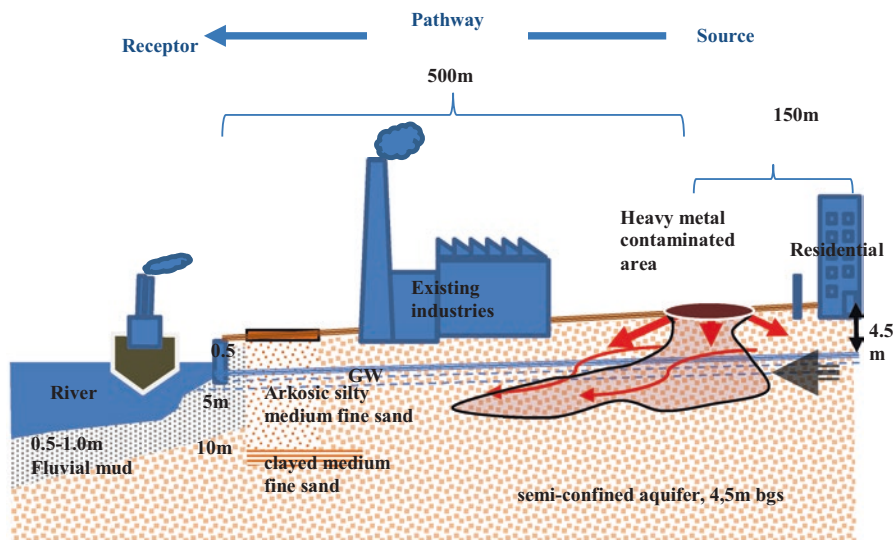


Fig. 4 Conceptual site model of the contaminated area

According to the available data, the conceptual model of the site can be summarized as presented in Fig. 4, regarding the water flow direction, the position of the contaminated area, and the progressive contaminants dispersion.

From the conceptual model for the contaminated zone, an injection plan/monitoring was implemented not only to allow the assessment of the downstream effect and through the groundwater flow direction, but also in the opposite direction, upstream, evaluating the mobilization capacity of the nanoparticles in different directions from the injection point.

4.1 Baseline Situation: Soil Contaminants

In order to make a preliminary assessment of the main contaminants in the soil (characterization of existent contaminated situation), three drillings boreholes (S1, S2, and S3) were conducted at the pilot test site (Fig. 5), with full and continuous soil sampling by “Direct Push” method (ASTM D6282 05).

The soil samples were collected in the unsaturated zone, until 4.0 m deep. The samples were collected inside transparent liner tubes of 100 cm long (Fig. 6). Further investigations were made and samples from selected liner sections were submitted to chemical evaluation.

Taking into account the history of the local contamination, and that the processes of migration of the contaminating compounds were made in the first few meters below the surface, it was decided to investigate the more superficial horizons. The



Fig. 5 Location of the preliminary drilling investigation campaign



Fig. 6 Different phases during the sampling process using the direct push soil sampling procedure

horizons to investigate were selected considering the depth and proximity to the water table, which varies from 4.5 to 5.0 m deep. Two layers of analysis were considered:

1. a shallower horizon between 0.5 and 1.0 m
2. a more profound horizon within the 3.0–3.5 m

In the following Table 2, it can be seen the main heavy metal pollutant compounds distribution, present in the soils of the investigated area.

Table 2 Main pollutant compounds at different depths for the drilling investigation points

Pollutant compounds	Boreholes					
	S1 (0.5– 1.0 m)	S1 (3.0– 3.5 m)	S2 (0.5– 1.0 m)	S2 (3.0– 3.5 m)	S3 (0.5– 1.0 m)	S3 (3.0– 3.5 m)
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Ar	72	11	8.1	220	4	3700
Ba	300	14	67	17	16	19
Cr	5.3	9.7	5.8	7.2	9.4	15
Pb	190	18	220	44	6.3	320
Zn	270	46	83	49	110	6600
V	6.2	16	7.8	12	10	16
Cu	920	210	440	270	160	4300
Co	23	N.I	N.I	N.I	N.I	15
Sb	9.2	N.I	N.I	N.I	N.I	N.I
Sn	N.I	N.I	11	N.I	N.I	N.I
Ni	N.I	3.9	N.I	N.I	3.4	N.I

N.I not identified

4.2 Laboratory Evaluation on the nZVI Application Effectiveness

Prior to the field work, laboratory tests were developed that could anticipate the behavior of nZVI when applied in the field, while at the same time assessing the most appropriate concentrations to be applied, taking into account the type of contaminants and the effect of reducing these contaminants downstream of the circuit.

The aim of the laboratory work was to perform long-term (2 months) kinetic and concentration tests on the nZVI effectiveness in degrading a contaminant cocktail (inorganic contamination by heavy metals) present in water and soil samples from the study area.

The laboratory tests have been performed over four soil samples collected at two depth intervals (1.0–1.5 m and 3.0–3.5 m) and over groundwater samples taken from two wells—PZ2 and PZ4 (Fig. 12).

The soil was stored at a temperature of 8 °C until it was used in analytical preparations for chemicals tests. Approximately 12 L of water was collected from the site, transported to the laboratory and subsequently stored in cold storage at a temperature of 8 °C.

The laboratory tests were performed on soil samples collected in two boreholes made during the instrumentation of the field test area, taking up two depth ranges (1.0–1.5 m and 3.0–3.5 m) to obtain four soil samples and on groundwater samples collected from two installed piezometers (PZ2 and PZ4, see Fig. 12).

The contaminated soil, without previous drying, was dosed with water in the mass ratio of 1:2, i.e., approximately 350 g of soil for 700 mL of water. The mixture was homogenized in a mechanical shaker [19] (Fig. 7).



Fig. 7 General aspect of the mechanical shaker device

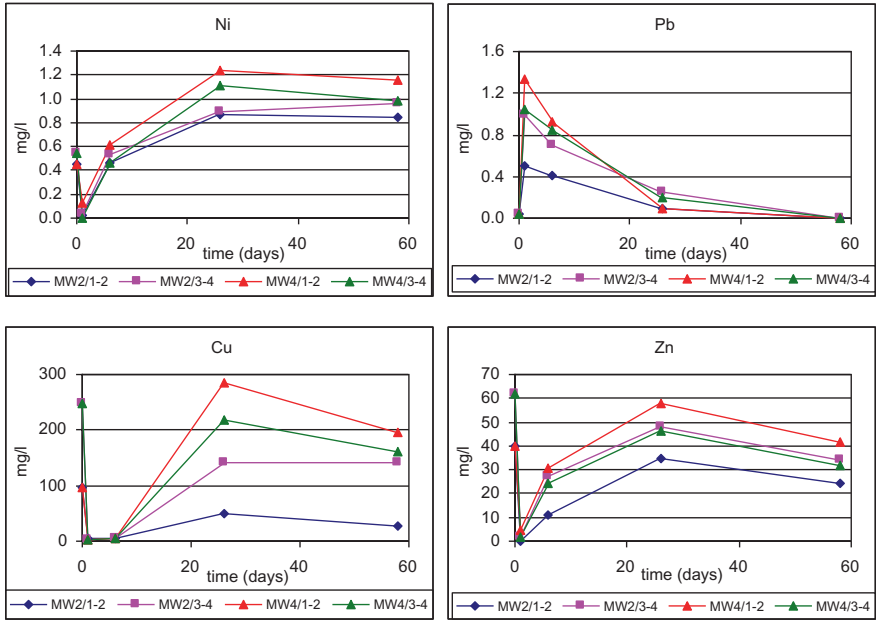
Kinetic batch tests with water and soil were performed for three different concentrations of nano-iron (0.3, 1.4, and 7.1 g/L). A sufficient number of sampling containers were prepared so that enough samples could be collected to perform analysis in a total of four time steps from the nZVI application—i.e., after 24 h, and then after 6, 26, and 58 days. Liquid phase samples were taken from the blank samples⁸ and from the sample container with the nano-iron, in each time step. During the sample collection, pH and Oxidation Reduction Potential (ORP) measurements were taken in the liquid fraction.

The nZVI particles used in the laboratory tests were supplied by NANOIRON, s.r.o, having a trade name of NANOFER 25S. These nanoparticles were also used in the site tests performed in Barreiro. The technical specifications of the NANOFER25S are summarized in Table 1.

The laboratory tests showed that an important decrease in heavy metals concentrations on the samples was achieved when 1.41 and 7.1 g/L nZVI concentrations were used. As an example of the heavy metal concentrations changes, the following graphs reveal the effective evolution along 58 days (Figs. 8 and 9).

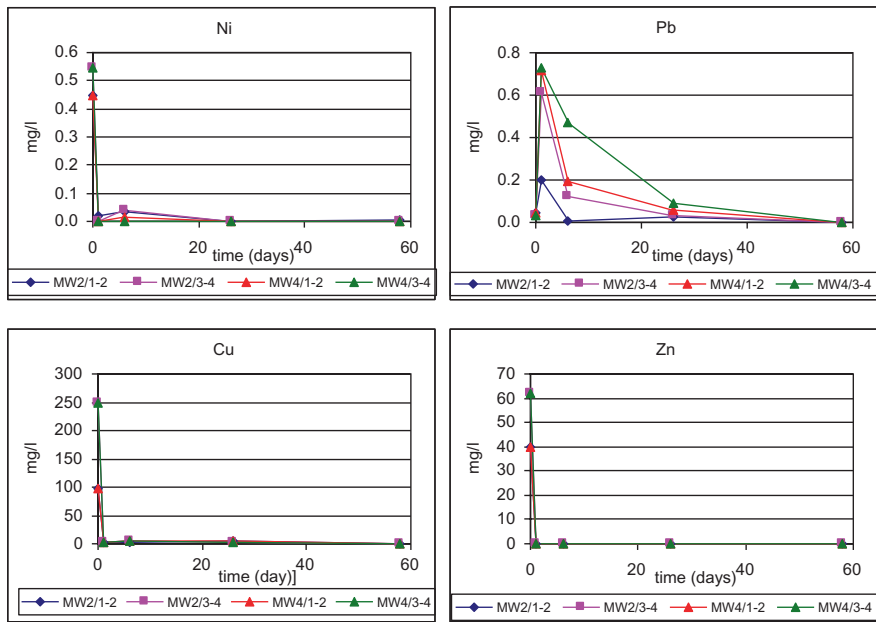
All metals (except Pb) are initially reduced by the initial dose of iron in the amount of 1.4 g/L. Some of metals are even reduced below the detection limit. However, the observed concentration decrease was not permanent, and the concentration rebound has been monitored up to their initial values for a major part of metals.

⁸ Blank sample, as considered in the tests performed by Aquatest. a.s (www.aquatest.cz), refers to the water samples collected on site, before nZVI injections.



Kinetics of heavy metal concentrations changes in samples with 1,4 g Fe/L.

Fig. 8 Results for a 58 days period, for 1.4 g/L nZVI addition in the four lab tested samples. Kinetics of heavy metal concentrations changes in samples with 1.4 g Fe/L.



Kinetics of heavy metal concentrations changes in samples with 7,1 g Fe/L.

Fig. 9 Results for a 58 days period, for 7.1 g/L nZVI addition in the four lab tested samples. Kinetics of heavy metal concentrations changes in samples with 7.1 g Fe/L.

Figure 9 shows the result of the efficient and permanent nZVI dose (7.1 g/L). Again the exception in heavy metals behavior shows Pb which is initially released from the soil to the water (the initial concentration increase) and afterwards is slowly removed from the water.

The initial increasing of the Pb concentration could not be explained by polluted nZVI addition because its concentration is independent from the dosed nZVI concentration. Based on the obtained laboratory results, a few recommendations were issued considering the next step by applying the nZVI on site.

From the evaluation of the analysis of the liquid phase, it can be stated that:

- The substantial part of applied nZVI is consumed on low groundwater pH neutralization.
- In this case it would be more efficient to provide pH neutralization by cheaper and more efficient, buffering amendment.
- The efficient concentration for the present system was evaluated in order to balance between 3 and 4 g/L (with equivalent values 6–8 g/kg of contaminated soil), however and considering the renewal of the natural system, by the reentry of more contaminants, resulting from the dynamism of the system itself, it is prudent to admit that the concentration of nZVI to be applied can be higher. And this has been demonstrated in the effectiveness revealed for higher concentrations of nZVI in the system.

4.3 Site Injection Method and Monitoring

4.3.1 Definition of the Testing Areas

The test site was divided into three zones—Zone I, II, and III (Fig. 10), with distinct dimensions and purposes, resulting from the interactive procedures and obtained results:

- Zone I—72 m² (6 m × 12 m)—Evaluation of the saturated zone
- Zone II—54 m² (9 m × 6 m)—Evaluation of the saturated zone
- Zone III—36 m² (6 m × 6 m)—Evaluation of the saturated zone

The Zones I and II were defined based on the observed contaminant's concentration, taking in consideration the influence of the S2 and S3 drilling areas, to evaluate the nZVI injection effects in the saturated zone.

The Zone III was defined later, located between the first two zones, for an nZVI evaluation effect, considering also the injection process in the saturated horizon, but now with a higher nanoparticles concentration, following the main directives provided by the previous laboratory phase.

Based on information, gathered from previous sampling and monitoring campaigns, it was assumed that the hydrodynamic flow in the tests area runs to North and Northeast, with an average speed of 30 m/year. The injection points and the piezometers position in Zones I, II, and III were defined considering these data.

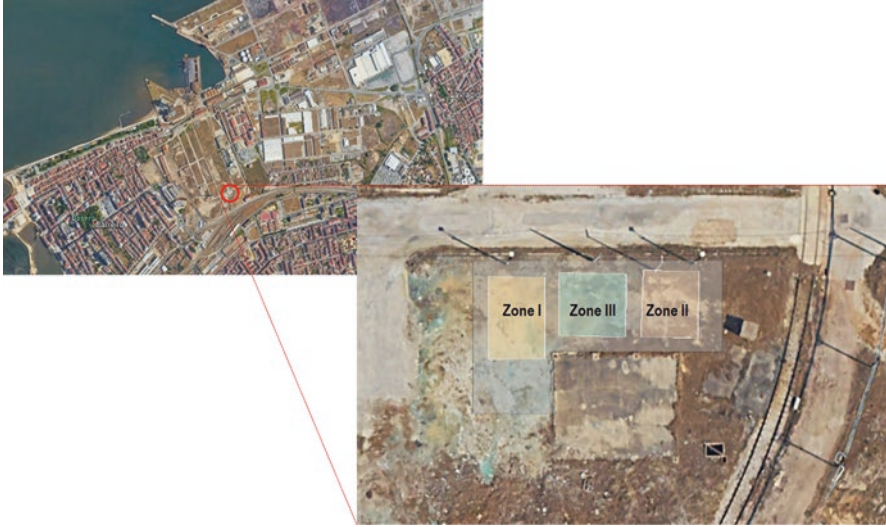


Fig. 10 Three different zones have been prepared for the nZVI application

For each area two distinct sections were defined: (1) one for *monitoring points*, which consisted of installed piezometers, from which water samples were collected, which would monitor the evolution of contaminants over time, after injection of nZVI, and (2) another relative to *injection points* that would be different in relation to the previous ones, depending on the type of evaluation that was intended for each zone.

4.3.2 Instrumentation

Piezometers were installed in the test areas, with a specific distribution in order to assess:

1. The nanoparticles mobilization capacity in saturated environments
2. The local hydrodynamic flow influence in the dispersion of nanoparticles
3. The relationship between nZVI concentrations in the injected solution and the decreasing of contaminants concentrations

The piezometers were installed in 6" diameter boreholes, opened with a hollow auger (Fig. 11). The groundwater level was found about 5 m deep. Piezometers were installed to a depth of 10.0 m, leaving the screen openings positioned between 4.0 and 9.0 m deep. HDPE 2" diameter pipes were used in the construction of the piezometers, with factory-set threaded caps and screen openings.

The space around the tubes was filled with calibrated gravel (fraction between 2 and 4 mm) from the base of piezometers to about 2.5 m from the surface. The sealing of the piezometers was carried out with bentonite, from 2.5 m depth to the



Fig. 11 Monitoring point's installation and general aspect of the Zone I field testing area

surface. Tight plastic lids were placed in the tops of the piezometers with the corresponding reference. All piezometers were developed before the nZVI injection, to ensure that the aquifer system balance was achieved soon after the installation process.

Knowing the limitations of the nZVI mobility and considering the effect of the low groundwater flow, it was decided to install the monitoring points at a maximum distance from the injection point of 3 m. The following Fig. 12 indicates the general distribution of the injection and monitoring points, for the three zones.

For the Zone I, nine piezometers (PZ) were installed downstream of the injection points (IP), and three piezometers were installed upstream. The piezometers were arranged in a square mesh of 3.0 m \times 3.0 m.

In Zone II, considering the possibility of occurring radial dispersion from the injection points, the monitoring points were arranged on a semi-circle, leaving a single monitoring point upstream.

In Zone III, six piezometers were installed, three of them downstream of the injection point and the other three upstream. The piezometers were spaced 3.0 m in between, and arranged in two rows, 6.0 m distanced. The assembly of only six piezometers in the immediate vicinity of the injection points took into account the results of injections made previously in Zones I and II, which proved the reduced nZVI mobility slightly beyond 3 m distances.

In order to validate the local geological and hydrogeological model and to determine the factors that control the transport mechanisms and dispersion parameters, the use of lithium/bromine tracers took place in Zone I.

It should be noted that before the injection of nZVI, all the monitoring points were properly developed so that the aquifer system could reach the equilibrium and effectively translated the underground water circulation, after the piezometers



Fig. 12 General aspect of the field testing area, and monitoring point’s distribution for the three zones

installation. In this way, any cross-disturbance effects imposed by the drilling process were reduced.

4.4 The nZVI Application

4.4.1 Equipment

The nZVI injection was made using a rig mounted on a tracked chassis, equipped with percussion devices for crimping a probe. The injection probe used was pressure activated (provided by GeoProbe) with four nozzles and one non-return valve. It was coupled to hollow rods of 1.5 m long with threaded sections. The extent necessary to achieve the programmed depth for each injection was obtained by coupling rods in sequence (Fig. 13).

The nZVI solution was injected under pressure, with the support of a GeoProbe pump GP300, keeping an injection pressure of about 5 bar (Fig. 13a).

Using a mechanical drilling rig adapted for the injection process, the nZVI were injected at different depths, in the saturated horizon using different slurry concentrations for the different zones—1, 3, and 7 g nZVI/L of water (Fig. 13b) (see Sect. 4.4.3).

Considering the direction of the groundwater flow, it was decided to inject in a middle point which would be at the same distance between the upstream and downstream monitoring points (Fig. 14).



Fig. 13 (a, b) General aspect of the nZVI injection device



Fig. 14 General view of the Zones I and III, respectively

Therefore the distribution of the monitoring points to evaluate the injection method effect was 3 m distance between monitoring wells (Fig. 15).

It was intended, with this methodology, to create a reactive barrier that could somehow contain the downstream migration of the heavy metals: (1) by their immobilization when aggregating into multidimensional structures, (2) or by their decomposition or transformation into less reactive and therefore less polluting elements.

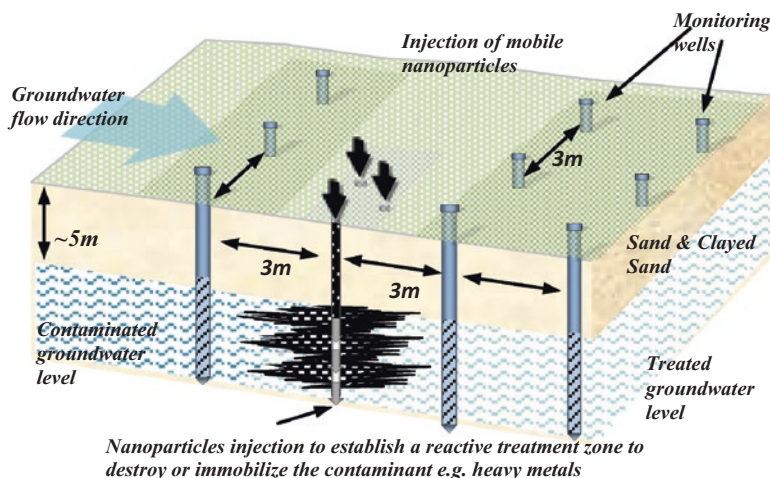


Fig. 15 Scheme of nZVI application procedure [20]

4.4.2 Dosage

As previously referred, different nZVI concentrations were injected in the three described areas, to evaluate mobility and contaminants concentration decrease on soil and groundwater.

As mentioned before and taking into account the laboratory tests results, the solutions injected below the saturated zone had 1 g nZVI/L water, 3 g nZVI/L water, and 7 g nZVI/L water.

The process of preparing the solution to inject took place at the test site, using bottom agitator pumps to keep the solution in the tanks thoroughly mixed before injection. The water used in the solution preparation was water from the public supply system, in order to not introduce into the system another variable that would make the entire application process more complex and expensive.

4.4.3 Injection

The injection process ran continuously at each point until the pre-set amount was injected. For this procedure, three technician teams were deployed, working continuously in 8-h shifts.

A synthesis of the injection quantities procedure in each test area is presented in the following Table 3. It should be noted that the nanoparticles transport efficiency depends on the characteristics of the groundwater flow. That is why the nZVI injection occurred in the saturated zone.

Table 3 summarizes the characteristics of the solutions injected into each of the test zones.

Table 3 Description of the quantities, dosages, and date of the nZVI injection process, on each zone

	Zone I	Zone II	Zone III
Target	Saturated zone	Saturated zone	Saturated zone
Dosage (g nZVI/L water)	3	1	7
Injected quantity (L)	8000	12,000	8000
Number of injection points	2	2	2
Depth of injection and amount solution injected (L)	5 m–1.000	4 m–1.000	5 m–1.000
	6 m–1.000	5 m–1.000	6 m–1.000
	7 m–1.000	6 m–1.000	7 m–1.000
	8 m–1.000	7 m–1.000 8 m–1.000 9 m–1.000	8 m–1.000
Injection date	2010.12.11 up to 2010.12.28	2011.01.04 up to 2011.01.05	2011.07.23 up to 2011.07.27

4.4.4 Monitoring

The groundwater quality monitoring plan for I, II, and III Zones was based on the following sampling scheme:

- First sampling: reference situation/baseline—before the nZVI injection start, on the day of injection
- Second sample: 14 days after nZVI injection
- Third sample: 28 days after nZVI injection
- Fourth sampling: 56 days after nZVI injection
- Fifth sampling: 112 days after nZVI injection

Water sampling was carried out at 7.0 m deep within each of the installed piezometers and done by *Low Flow Sampling method* using a peristaltic pump. The following physical parameters were monitored by the *Flow Through Cell method*: temperature, pH, dissolved oxygen, and conductivity (Fig. 16).

In order to validate the local hydrogeological model and determine the factors that control the transport mechanisms and dispersion parameters, lithium/bromine tracers were applied in Zone I.

Given the disposition of the different monitoring points (PZ) and considering that the groundwater flows from south to north, parallel to the alignment set by the injection point and the central PZs, the tracer was added inside PZ8. A sampling program was carried out in PZs 4, 5, and 6, on April 21st 2011, 37 days after the tracer injection, not having been detected any change in lithium/bromine concentrations before and after injection in those PZs. The observed fact supports the local hydrogeological data that refers to a water flow average speed of ≈ 30 m/year.



Fig. 16 Site water sampling procedure and water parameters monitoring

Table 4 Main activities calendar

Actions	Zone I	Zone II	Zone IV
	(GW samples)	(GW samples)	(GW samples)
Sampling for the reference situation	2010.12.21	2010.12.27	2011.07.22
nZVI injection date (not continuous)	2010.12.22 up to 2010.12.28	2011.01.04 up to 2011.01.05	2011.07.23 up to 2011.07.27
First sampling after injection (14 days)	2011.01.10	2011.01.25	2011.08.10
Second sampling after injection (28 days)	2011.01.24	2011.02.08	2011.08.24
Third sampling after injection (56 days)	2011.02.21	2011.03.09	2011.09.22
Fourth sampling after injection (112 days)	2011.04.21	2011.05.09	2011.11.16

GW groundwater

4.4.5 Main Actions Calendar

Table 4 evidences the main activities performed, and the subsequent sampling program.

4.5 Results

The results of water samples tests collected at Zones I, II, and III show significant differences in metals concentrations (before and after nZVI injections), particularly in the monitoring wells located nearby the injection points (3 m). By contrast, in the piezometers located more than 6 m from the injection points, the nanoparticles injection effect did not show a definite trend, which allows to conclude that the reactive effect of nZVI particles is only significant for distances which do not exceed 3 m from the injection point.

The average differences of the metal concentrations in water samples collected in Zones I, II, and III are slightly significant downstream the injection point, confirming the influence of water flow in the underground transport of nanoparticles. These slight differences are probably related with the low transmissivity in the testing area.

Table 5 shows the proportions between the elements average value before and after the nZVI injection on three piezometers located downstream of the injection points, in water samples collected in the I, II, and III zones.

It appears that Zone I is the most suitable to establish the chemical mechanisms sequence that occurs with the nZVI injection (this area is also the better instrumented and where, therefore, can be better established the connection with the underground water flow). In Zone I there is, even slightly, an initial decrease of sulfates, although the values will recover at the end of 56 and 112 days. Correspondingly, the values of Co and, secondarily, Cd, decrease, recovering thereafter. In Zn case, this effect is less pronounced, but the pattern is similar. Cu tends to initially increase and then decreased. In this area, there is the notable exception of As, which undergoes a sharp increase after the nZVI injection.

It appears that there is a temporal sequence relatively constant on each sampled point in Zone II, tending to decrease regarding the metal concentration over time, also with the Arsenic exception.

In Zone III it is observed the arsenic reduction but, instead, other elements rise dramatically in terms of concentrations (e.g., Cu), presented some of them an erratic behavior over time. A justification could probably focus on the fact that this metal could have been released from soil to water, but its complete reduction by nZVI has not occurred. In this context, a new injection could have facilitated its continuous reduction, effectively creating a reactive barrier to its mobilization.

In this pilot study it was found that there is a decrease in tendency of a part of the sulfate concentration into the aquifer system after the injection of nZVI, which usually correlates with a decrease of several metals in solution. This correlation may suggest that the effect of nZVI induces the ion sulfate reduction and subsequent precipitation of metals as metastable sulfides. However, it is noticed that the pH tends, however, to decrease or maintain a low level so that the primary controlling mechanism will be, with high probability, the progressive oxidation of the Fe particles and consequent precipitation of the Fe(III) in hydroxide form. More than hypothetical sulfate reduction, the Fe hydroxide arrangement ensures the existence of solid phase with a high surface area and adsorption capacity, with which the soluble metals have high affinity.

The Fe concentrations consistently show an initial peak (injection) followed by a more or less pronounced break, to consistently low levels. This pattern indicates the progressive Fe oxidation and dispersion, which, depending on the redox potential, tends to precipitate from the solution. These effects tend to spread in different areas in response to the groundwater flow direction.

One of the observed characteristics is a pronounced reduction of the chemical oxygen demand in the water samples, which suggests that organic compounds are

Table 5 Ratios between average element concentrations before (index 100) and after nZVI injection, in water samples from three downstream monitoring wells (values in %, except pH)

Area	Days	Ammonia as N	Ammonia and ammonium ions	Chemical Oxygen Demand (COD)	Nitrates	Nitrites	Sulfate as (SO ₄ ²⁻)	Aluminum (Al)	Arsenic (As)	Cobalt (Co)	Nickel (Ni)	Lead (Pb)	Manganese (Mn)	Copper (Cu)	Zinc (Zn)	Cadmium (Cd)	Selenium (Se)	Iron (Fe)	pH (absolute value)
Zone I	0	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	4.63
	14	0	0	115	5	461	79	54	631	0	0	24	52	114	61	78	35	40	5.03
	28	0	0	77	18	41	78	46	600	0	0	21	48	82	51	62	27	37	5.04
	56	0	0	54	9	12	90	36	631	0	0	15	39	75	45	47	29	27	4.86
	112	45	45	62	48	73	105	74	131	65	78	45	85	68	72	97	101	26	4.64
Zone II	0	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	3.65
	14	142	142	85	812	158	81	54	66	60	70	46	68	44	70	63	85	0	3.59
	28	142	142	46	655	180	96	93	133	93	106	54	101	76	110	102	117	0	3.61
	56	117	117	38	334	86	66	85	215	90	103	38	97	68	103	97	115	0	3.59
	112	125	125	85	707	32	78	87	233	80	94	62	90	63	95	82	88	319	3.65
Zone III	0	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	4.79
	14	32	32	111	113	126	138	202	110	201	96	88	68	438	127	105	135	14	4.07
	28	34	34	133	68	102	139	209	50	211	100	119	70	432	130	101	100	22	4.01
	56	37	37	100	107	38	135	225	50	209	102	123	66	459	136	102	110	15	3.84
	112	47	47	89	253	42	120	171	50	156	74	73	49	356	100	60	100	0	3.74

being degraded by reduction. The degradation of these compounds may explain the increase of the soluble Cu, since this metal has a high affinity for combining with organic compounds, unlike other metals such as Zn.

Other observed peculiarities, which still requires explanation, are that the injection tests in Zone I (3 g/L nZVI) have given better average results than observed in Zone III (7 g/L nZVI), contradicting the prior nZVI dosing laboratory study, where it was found that excessive Fe in the system would be essential to keep the redox balance, which stabilizes the solid phases where part of the soluble metals is fixed. Furthermore, the mechanisms for subsequent Fe oxidation and consequent Fe hydroxide form precipitation, decreases the environment's pH (particularly well noticed in Zone III results).

However, the pH decrease tends to disfavor the metals (cationic) adsorption on the hydroxides surfaces, with the exception of the As, which forms anionic complexes in solution. The metals adsorption is significantly more favorable at alkaline pH and, in this sense, the pH values recorded for the Zone I (3 g/L) are slightly higher than those measured in Zone III (7 g/L). It follows that, on average, the best results came, from other motives, by the environment pH value.

The evolution of some major pollutants was favorable with a sharp decrease in the first days after the application of nZVI, assuming that this effect was mainly due to the significant reactivity which occurred immediately after injection (see tendency lines, Fig. 17), clearly noted on the piezometers near the injection point [3].

Despite the significant amount values for all the monitoring points available for consultation, in this work it was intended to highlight the most relevant aspects, considering the initial value as the baseline obtained from collected water samples in the three zones, between the average concentrations of elements before and after the nZVI injection in the three piezometers downstream of the injection point.

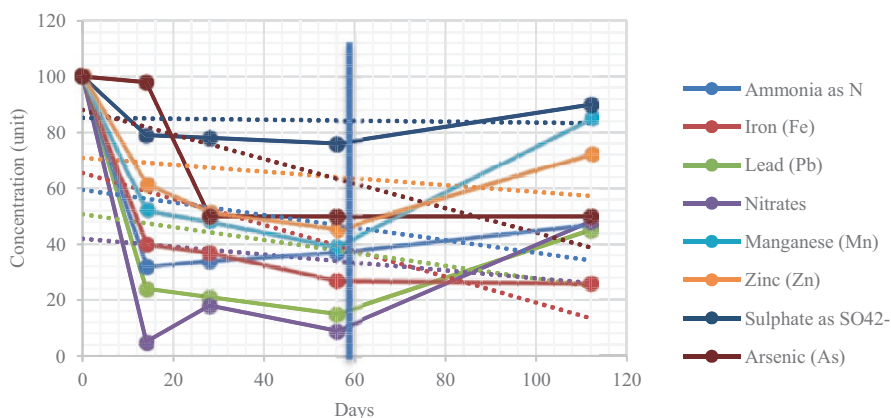


Fig. 17 Time evolution of some of the contaminants' concentration, and half period milestone

It is observed also after a significant decrease in the concentration of most heavy metals, there was a stabilization of the values which reflects also a stabilization of the reducing effect caused by nZVI.

Considering the half time of the investigation process and for almost all the referred elements, the reducing concentration of each element passes over 60% below the initial concentration. However it is observed in a comprehensive way, and after several weeks of monitoring, an elevation of contaminants to levels close to the initial, but still below baseline values, contributed to the renewal effect that this type of hydrogeological system provides (Fig. 7). In this pilot study, it was found that there is a tendency to decrease the concentration of a part of the sulfate in the aquifer after the injection of nZVI, which usually correlates with a decrease of various metals in solution. The effect of the nZVI was reflected in the sulfate ion reduction and subsequent precipitation of the metals as sulfides.

As mentioned before, the progressive oxidation of the Fe particles and consequent precipitation of Fe(III) in the hydroxide form, rather than the hypothetical sulfate reduction, iron hydroxides formation ensures the existence of a solid phase with high surface area and adsorption capacity with which the metals in solution have high affinity.

The metal's adsorption is more favorable in alkaline pH. The recorded values revealed that the pH increase has influenced the nanoparticles' degrading action for some of the present metals.

Moreover, the pH increase is due to the reductive action of nZVI, acting not as the metals reducing agent but as a hydrogen source.

In these more aggressive environments, the corrosion effect of nanoparticles occurs, limiting their functionality.

5 Conclusions

Despite the minor effect of the nanoparticles in some contaminants elements, it was observed that this kind of methodology for the soils and groundwater remediation purposes act in real time reducing the available concentration of these heavy metals. Some recent studies have described the surrounding environment as the main responsible for the less expected effect of the nZVI in the remediation process, whether related with the renovation of the general environmental system or with the remobilization of the chemical elements due to the injection or simple delivery process of the nZVI solution.

The increasing of the contaminant elements concentration, in this particular case, after 4 months of monitoring, is due to the renovation of the hydraulic system which have contributed to the renovation of the leachate process and so to the heavy metals transport into the aquifer. The corrosion effect of the low pH of the Barreiro groundwater aquifer, degraded rapidly the nZVI which have contributed also for the less expected effect on the nanoparticles heavy metal removal. It is possible to increase

the local pH by adding a hydroxide as the $\text{Ca}(\text{OH})_2$ or $\text{Na}(\text{OH})$, creating a better environment for the effective reaction of the nanoparticles and consequently a more effective remediation process of the natural ground and aquifer system, which will also increase the costs of all remediation process.

Despite all described actions and satisfactory preliminary results, it is important to continue these investigation processes by using different nanoparticles in eventual different contaminant contexts and the Industrial Barreiro site could be a large-scale laboratory for these kind of investigation purposes.

An optimization of the nanoparticles effect on the heavy metal soil and ground-water contamination may pass by using a cocktail of different products based on nZVI or other, but with more resistance and maintenance in the environment, increasing the possibility of a more durable effect on the degradation of contaminants.

Recent laboratory studies gave quite interesting answers and guidelines for this important and useful method for soils and groundwater remediation.

The urgent need for low-cost and effective solutions that enable the in situ recovery of contaminated sites, implies the necessity of using new technologies with efficiency and low impact on the surrounding environment. The use of nZVI is one of the possible new approach options.

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